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Method of preparing rigid polyurethane foam

5 The present invention relates to a method of preparing a rigid polyurethane foam and an apparatus for preparing a rigid polyurethane foam. The rigid polyurethane foam can be used as heat insulation materials for freezer, refrigerator, building and the like.

10 Rigid polyurethane foams are widely used as heat insulation materials for refrigerator-freezer, for example, refrigerators for household use, since they have a low product density, excellent heat insulating properties and a high mechanical strength.

15 As blowing agents for preparing the rigid polyurethane foams, chlorofluorocarbons (hereinafter referred to as CFCs), in particular trichlorofluoromethane (CFC-11), have been conventionally used.

20 However, since the CFC-11 blowing agent contains halogens, there is apprehension that it may deplete the ozone layer and cause the environmental issues such as global warming. For the purpose of protecting the global environment, the amounts of production and consumption of CFCs are now under international regulations. In Japan, the production of CFCs had been prohibited by the end of 1995. As substitute new blowing agents, hydrochlorofluorocarbons (HCFCs) having a low ozone depletion potential are used. For example, HCFC-141b (1,1-dichloro-1-fluoroethane), HCFC-22 (chlorodifluoromethane), HCFC-142b (1-chloro-1,1-difluoroethane) have been introduced and applied as blowing agents.

However, use of HCFCs, the substitute for CFCs, are now phased down, because they also contain chlorine atom in their molecules and therefore still retain the property of depleting the ozone layer although their effects on the ozone layer are little. Thus, in terms of global environmental protection, use of blowing agents having no effects on the ozone layer depletion at all was newly proposed. Hydrocarbon-based blowing agents which contain no chlorine atom and pose no risk

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of depleting the ozone layer, for example cyclopentane, have already been introduced and applied for some purposes.

5 However, although cyclopentane is most suitable as an earth-friendly blowing agent, it involves some drawbacks. In particular, gaseous cyclopentane itself has a high thermal conductivity and the heat insulating performance of the rigid polyurethane foams employing cyclopentane is therefore inferior to those employing conventional HCFC-141b. Accordingly, there is a need for improving the heat insulation characteristics of such rigid polyurethane foams.

10 The present invention provides a method of preparing a rigid polyurethane foam from

- 15 (1) an organic polyisocyanate comprising an aromatic polyisocyanate,
- (2) a polyol comprising a polyether polyol and/or polyester polyol,
- (3) a blowing agent, and
- 20 (4) a surfactant, a catalyst and other auxiliaries,

characterized in that

25 the blowing agent (3) is cyclopentane and water,

the polyol (2) is a polyether polyol and/or polyester polyol having poor compatibility with cyclopentane, and

30 cyclopentane is mixed and dispersed in a polyol premix comprising the components (2) to (4).

The phrase "having poor compatibility with cyclopentane" means that the solubility of cyclopentane in the polyol is 20 g or below, for example 10 g or below, and particularly 5 g or below. The term "solubility" means the number of grams of cyclopentane which are soluble in 100 g of the polyol at 25°C.

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In order to mix and disperse cyclopentane in the polyol premix, it is preferred to use a stirrer of which circumferential speed is at least 5 m/s. In order to allow the dispersed liquid to exist stably in the tank of the foaming machine, it is preferred to stir the mixture at a circumferential speed of at least 0.5 m/s and circulate the mixture through a static mixer.

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The present invention provides a composition for preparation of a rigid polyurethane foam, comprising

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(1) an aromatic polyisocyanate,

(2) a polyether polyol and/or polyester polyol,

(3) a blowing agent comprising a mixture of cyclopentane and water, and

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(4) a catalyst, a surfactant and other auxiliaries,

and further provides a method of preparing a rigid polyurethane foam from said composition by mechanically disperse cyclopentane in the polyol premix comprising the components (2), (3) and (4).

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As the aromatic polyisocyanate (1), for example, polyisocyanates such as tolylene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), and polymethylene polyphenyl polyisocyanate (polymeric MDI), or modified polyisocyanates thereof can be used alone or in combination with each other.

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Modified polyisocyanates, that is, products obtained by partial chemical reactions of organic di- and/or polyisocyanates may be used. For example, di- and/or polyisocyanates containing an ester, urea, biuret, allophanate, carbodiimide, isocyanurate and/or urethane group can be used.

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The NCO content of the aromatic polyisocyanate (1) is preferably 30 to 50% by weight, for example, 30 to 33% by weight.

The polyol (2) is a polyether polyol and/or polyester polyol.

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The polyether polyol may be obtained by addition polymerization of propylene oxide and/or ethylene oxide using a polyhydric alcohol such as ethylene glycol, propylene glycol, glycerine, trimethylolpropane, pentaerythritol, sorbitol, sucrose, or bisphenol A, an aliphatic amine such as triethanolamine or ethylenediamine, or an aromatic amine such as toluenediamine or methylenedianiline (MDA) as a starting material.

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The polyether polyol may be obtained by a known method, for example, by anionic polymerization of an alkylene oxide using a starting material containing 2 to 8, preferably 3 to 8, reactive hydrogen atoms in its molecule, with using an alkali hydroxide such as potassium hydroxide or sodium hydroxide or an alkali alcoholate such as potassium methylate or sodium methylate as a catalyst. Alternatively, the polyether polyol may also be obtained by cationic polymerization of an alkylene oxide using a Lewis acid such as antimony pentachloride or boron fluoride etherate as a catalyst.

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Suitable alkylene oxides are tetrahydrofuran, ethylene oxide, 1,3-propylene oxide, 1,2- or 2,3-butylene oxide, 1,2-propylene oxide, and styrene oxide. Ethylene oxide and 1,2-propylene oxide are particularly preferred. These alkylene oxides may be used alone or a mixture thereof.

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Examples of the reaction starting material are polyhydric alcohols such as ethylene glycol, propylene glycol, glycerin, trimethylolpropane, pentaerythritol, sorbitol, sucrose, and bisphenol A, or alkanolamines such as ethanolamine, diethanolamine, N-methyl- and N-ethyl-ethanolamine, N-methyl- and N-ethyl-diethanolamine, tri-
5 ethanolamine, and ammonia.

In addition, aliphatic amines and aromatic amines may be used as the reaction starting material. Examples are ethylenediamine, diethylenetriamine, 1,3-propylenediamine, 1,3- or 1,4-butylenediamine, 1,2-, 1,3-, 1,4-, 1,5-, and 1,6-hexamethylenediamine, phenylenediamine, o-toluenediamine, m-toluenediamine, methylenedianiline (MDA), and polymethylenedianiline (P-MDA).
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The polyether polyol preferably contains 3 to 8, especially preferably 3 to 6, functional groups, and those having a hydroxyl value of 300-800 mg KOH/g, more preferably of 300-500 mg KOH/g, are suitable.
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As the polyester polyol, a polyester polyol prepared from a polycarboxylic acid and a polyhydric alcohol, such as polyethylene terephthalate, can be used. A suitable polyester polyol may be prepared from an organic carboxylic acid (particularly dicarboxylic acid) having 2-12 carbon atoms and a diol preferably having 2-12 carbon atoms, especially preferably 2-6 carbon atoms.
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Examples of such organic carboxylic acid are succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, maleic acid, phthalic acid, isophthalic acid, and terephthalic acid. Instead of a free carboxylic acid, corresponding carboxylic acid derivatives, for example dicarboxylic acid monoester or diester of an alcohol having 1-4 carbon atoms or dicarboxylic anhydride, may also be used.
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As the diol, ethylene glycol, diethylene glycol, 1,2- or 1,3-propanediol, dipropylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, or 1,10-decanediol may be
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used, and glycerine or trimethylolpropane may be used as a triol. Similarly, lactone-based polyester polyols may also be used.

5 The polyester polyol preferably contains 2 to 3, especially preferably 2, functional groups, and those having a hydroxyl value of 200-600 mg KOH/g, preferably of 350-450 mg KOH/g, are suitable.

10 It is preferred that at least part of the polyol, in particular at least 10% by weight of the polyol, for example at least 30% by weight, is a polyether polyol prepared by addition polymerization of ethylene oxide and propylene oxide to an initiator such as sorbitol.

15 As the blowing agent (3), a combination of cyclopentane and water is used. The amount of water used herein is 0.1 to 5 parts by weight, preferably 0.1 to 1 part by weight, per 100 parts by weight of the polyol. The amount of cyclopentane is preferably 5 to 30 parts by weight, more preferably 10 to 25 parts by weight, per 100 parts by weight of the polyol.

20 As the catalyst, the surfactant and other auxiliaries, those conventionally known may be used. Amine catalysts or metal catalysts may be used as the catalyst.

25 As the amine catalyst, a tertiary amine such as triethylenediamine, tetramethylhexamethylenediamine, pentamethyldiethylenetriamine, or methylmorpholine can be used.

30 As the metal catalyst, an organic metal compound such as stannous octoate, dibutyltin dilaurate, or lead octylate can be used. The amount of the catalyst is preferably 0.01 to 5 parts by weight, more preferably 0.05 to 2.5 parts by weight, per 100 parts by weight of the polyol.

As the surfactant, usual organic silicone-based compounds may be used. For example, L6900, SZ-1684, SZ-1689 or the like manufactured by Nihon Unicar Company Limited, F395 or the like of Shin-Etsu Chemical Co., Ltd., or B8465, B8474 or the like available from Goldschmidt may be used. The amount of the surfactant is 0 to 5 parts by weight, preferably 0.5 to 3 parts by weight, per 100 parts by weight of the polyol.

In the present invention, other auxiliaries such as foaming stabilizers, foam controlling agents, fillers, dyes, pigments, flame retardant additives, anti-hydrolysis agents may be used in appropriate amounts.

For preparation of polyurethane foam, the polyisocyanate and the polyol premix are injected into a mold to harden using a high pressure foaming machine. The NCO index of the polyisocyanate and the polyol premix may be 90 to 150, for example, 110 to 130.

Preferably, the high pressure foaming machine has a circulating line (for example, a high pressure circulating line) and a polyol tank.

The polyol premix is a mixture prepared by adding cyclopentane to a mixture of the polyol, the surfactant, the catalyst, water as a blowing agent and other auxiliaries, and mechanically mixing and dispersing them.

Although the stirrer for mechanically stirring the polyol premix may be any of usual stirrers, those having a circumferential speed of at least 5 m/s is preferred.

For example, cyclopentane may be mechanically mixed and dispersed by a stirrer having stirring wings of 7 cm in diameter at 1700 rpm (circumferential speed: 6 m/s), and fed into the polyol tank of a cyclopentane-compatible high pressure foaming machine having a static mixer in the high pressure circulating line.

A commercially available static mixer is sufficient for this purpose, and for example, a 1 inch x 8 blocks static mixer available from SULZER Corporation may be used.

5 On the other hand, the polyol dispersion liquid can stably exist by reasons that the circumferential speed of the stirrer of the polyol tank is at least 0.5 m/s and the circulating line of the high pressure foaming machine contains the static mixer.

10 By using such high pressure foaming machine, rigid polyurethane foams may be prepared by a prepolymer process or a one-shot process using a batch method or a continuous method. One particularly preferred method is a method of processing conducted according to a two-components process (Component A: isocyanate, Component B: polyol premix).

15 Components A and B are mixed at a temperature in the range of 15 to 35°C, and injected into a mold thermoregulated at 20 to 60°C (for example, 35 to 45°C), and foamed to give a rigid polyurethane foam.

20 The rigid polyurethane foam may be used as heat insulation materials for freezer, refrigerator, building and the like.

The present invention is further demonstrated by the following Examples and Comparative Examples.

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Cyclopentane Compatibility

Into a test tube, 100 g of a polyol is placed, a given amount of cyclopentane is added, and stirred and mixed thoroughly. After allowing to stand for one day, it is observed whether the mixture is clear, cloudy or separated. When the mixture is clear, the evaluation is "soluble". When the mixture is cloudy or separated, the evaluation is "insoluble".

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Compression Strength

The measurement is conducted using a universal tester (TCM 1000 manufactured by Minebea Co., Ltd.) according to JIS-A-9514.

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Core Foam Density

The core foam density refers to the density at the central part of the foam, and is calculated by measuring the weight down to 0.01 g and measuring the volume down to 0.1 cm³ by a water displacement method.

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Thermal Conductivity

The measurement is conducted on a 200 mm × 200 mm × 25 mm sample cut from the core of the foam, using a thermal conductivity tester (Auto Lambda manufactured by ELKO Instruments Trading, Co.) according to ASTM-C-518.

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Example 1

5 A polyol mixture liquid was prepared by adding an amine catalyst (1.8 parts by weight of tetramethylhexamethylenediamine plus 1.0 part by weight of pentamethyldiethylenetriamine plus 0.5 part by weight of trisdimethylaminopropyl-s-triazine), 2 parts by weight of a surfactant (L6900 manufactured by Nihon Unicar Company Limited), and 0.5 part by weight of water to 30 parts by weight of Polyol A, 25 parts by weight of Polyol B, 20 parts by weight of Polyol C, 20 parts by weight of Polyol D, and 10 parts by weight of Polyol E.

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To the polyol mixture liquid, 21 parts by weight of cyclopentane (blowing agent), was added, and mechanically mixed and dispersed by a stirrer having 7-cm stirring wings at 2,000 revolutions/min (circumferential speed: 7 m/s) to prepare the final polyol mixture. The polyol mixture liquid was fed into a high pressure foaming machine equipped with a static mixer (a 1 inch x 8 blocks mixer manufactured by SULZER Corporation), and mixed by circulating it at high pressure for a while. The solubility of cyclopentane was 5 g or below per 100 g of the polyols.

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According to the mixing ratio shown in Table 1, the polyol mixture and polymeric MDI were mixed and foamed. The urethane feedstocks were adjusted at the temperature of 20°C, and injected into a 600 mm x 400 mm x 50 mm aluminum mold adjusted at 45°C, and the molded product was demolded from the mold after 7 minutes. Physical properties of the molded product are shown in Table 1.

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Examples 2 and 3

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A polyol mixture liquid was prepared according to Table 1. As a silicone-containing surfactant, 2 parts by weight of F395 manufactured by Shin-Etsu Chemical Co., Ltd. was used. The other procedures were the same as those described in Example 1. Physical properties of the molded product are shown in Table 1.

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Comparative Examples 1 and 2

5 As in Example 1, a polyol mixture liquid was prepared according to Table 1. The mixture liquid was then mixed with cyclopentane, and fed into the high pressure foaming machine, and the molded product was obtained in the same manner as in Example 1. The difference between these Comparative Examples and Examples 1-3 is in that the polyol mixture liquid in these Comparative Examples was a liquid in which cyclopentane was completely dissolved. Physical properties of the molded product are shown in Table 1.

Polyol A:

15 A polyol obtained by addition of EO (ethylene oxide) and PO (propylene oxide) to sorbitol as a starting material, having a hydroxyl value of 550 mg KOH/g

Polyol B:

A polyol obtained by addition of PO to glycerin as a starting material, having a hydroxyl value of 520 mg KOH/g

Polyol C:

20 A polyol obtained by addition of EO to trimethylolpropane as a starting material, having a hydroxyl value of 550 mg KOH/g

Polyol D:

25 A polyol obtained by addition of PO to trimethylolpropane as a starting material, having a hydroxyl value of 865 mg KOH/g

Polyol E:

30 A polyester polyol derived from polyethylene terephthalate, having a hydroxyl value of 315 mg KOH/g

Polyol F:

A polyol obtained by addition of EO to ethylene glycol as a starting material, having a hydroxyl value of 374 mg KOH/g

5 Polyol G:

A polyester polyol derived from phthalic acid and diethylene glycol, having a hydroxyl value of 420 mg KOH/g

Polyol H:

10 Glycerin

Polyol J:

A polyol obtained by addition of PO to glycerin as a starting material, having a hydroxyl value of 390 mg KOH/g

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Polyol K:

A polyol obtained by addition of PO to toluenediamine/diethanolamine as starting materials, having a hydroxyl value of 450 mg KOH/g

20 Polyol L:

A polyol obtained by addition of PO to sugar/propylene glycol as starting materials, having a hydroxyl value of 380 mg KOH/g

Polyol M:

25 A polyol obtained by addition of PO to propylene glycol as a starting material, having a hydroxyl value of 500 mg KOH/g

Table 1

	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2
Polyol A	30	35	30	-	-
Polyol B	25	-	25	-	-
Polyol C	25	-	-	-	-
Polyol D	10	-	-	-	-
Polyol E	10	-	-	-	-
Polyol F	-	20	20	-	-
Polyol G	-	20	20	15	-
Polyol H	-	5	5	-	-
Polyol J	-	20	-	-	-
Polyol K	-	-	-	40	50
Polyol L	-	-	-	45	40
Polyol M	-	-	-	-	10
Cyclopentane	21	21.5	21.5	15.5	11.2
water	0.5	0.5	0.6	1.3	2.0
Polymeric MDI	170	130	130	123	140
Compressive strength (kg/cm ²)	2.0	1.5	1.6	1.5	2.0
Core foam density (kg/m ³)	35	32	32	32	35
Thermal conductivity × 10 ⁻⁴ (kcal/mh°C)					
25°C	163	161	162	163	173
10°C	154	155	156	158	168
0°C	150	151	152	156	166
Pentane compatibility (solubility: g)	Insoluble, ≤5 g	Insoluble, ≤5 g	Insoluble, ≤5 g	Soluble	Soluble

- 5 According to the present invention, a rigid polyurethane foam having a low thermal conductivity and excellent heat insulating properties can be prepared by using polyols having poor compatibility with cyclopentane.